JANUARY 23, 1984

CHEMICAL & ENGINEERING

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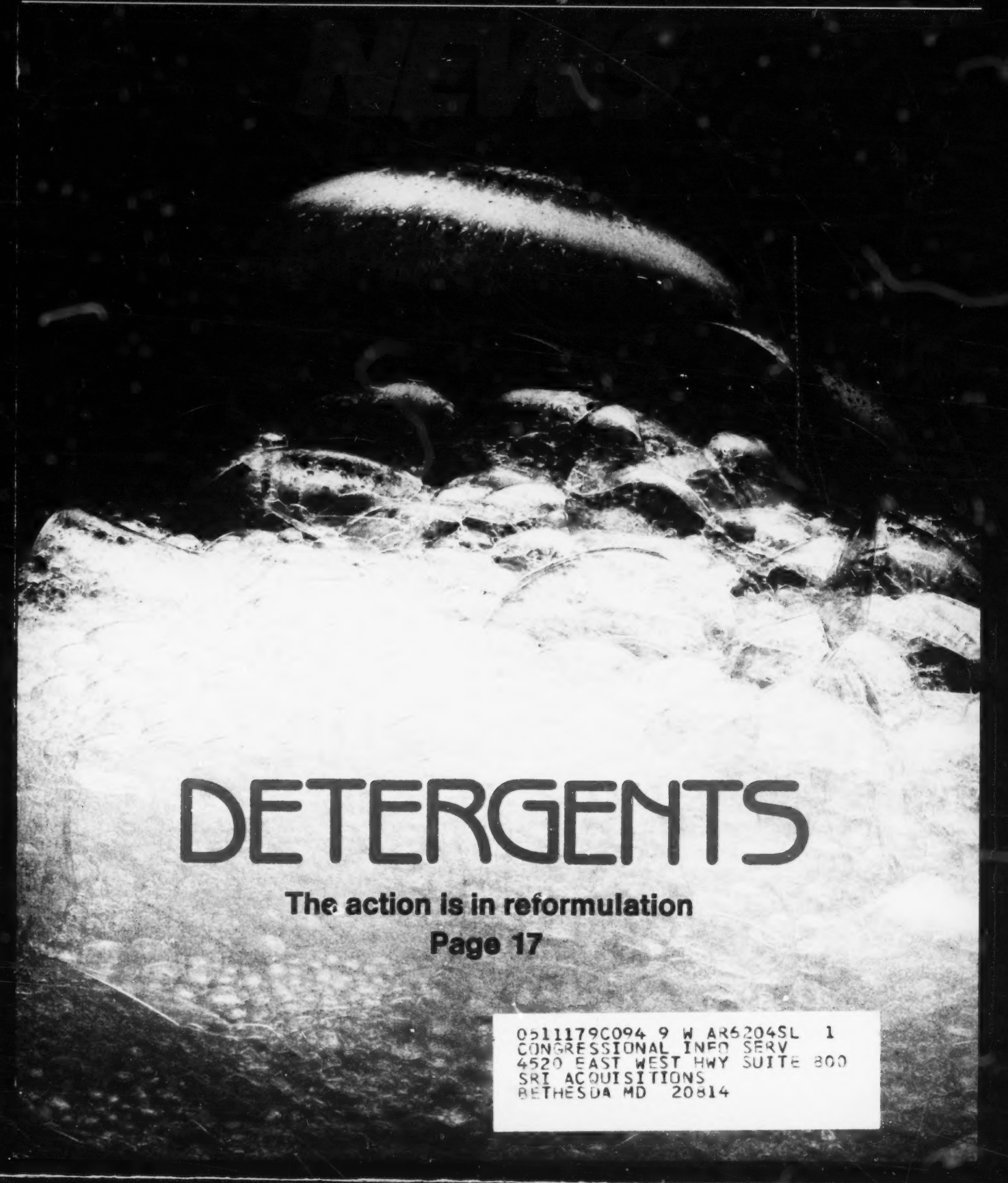

DETERGENTS

The action is in reformulation

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CHEMICAL & ENGINEERING NEWS

JANUARY 23, 1984

News of the Week

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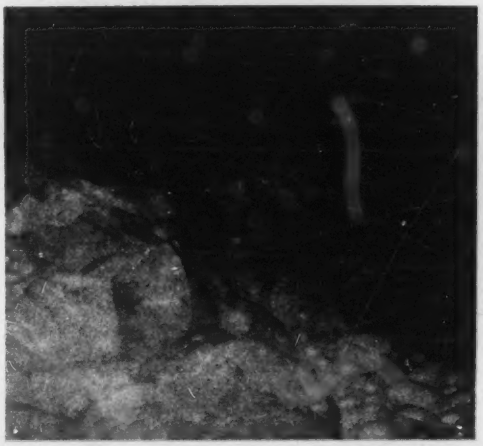


Detergent Report

Changes in formulations for detergents prompted by phosphate limits, cold-water washing affect chemical suppliers. **Page 17**

U.S. CHEMICAL TRADE: EEC threatens higher tariffs, quotas

Chemicals once again have become a pawn in a trade battle between the U.S. and the European Economic Community.

In retaliation against restrictions that President Reagan imposed last July on specialty steel imports from EEC countries, the community's governing commission has threatened to impose higher tariffs on some U.S. chemical exports and set quotas on others. The EEC action will become effective March 1, unless officials in the Office of the U.S. Trade Representative (USTR) can come up with a satisfactory package of trade concessions to compensate EEC for the curbs against its specialty steel shipments.

The higher tariffs will hit U.S. exports of methanol and vinyl acetate to EEC countries. Quotas are targeted against styrene and certain grades of polyethylene sheet.

The duties on both methanol and vinyl acetate will increase almost 50%. For methanol, the tariff will rise from 13.5% to 19.9% by adding a 6.4% surcharge. The vinyl acetate duty will jump from 13.2% to 19.6%. These rates of duty, however, will be effective only in 1984. As a result of agreements reached earlier during the Tokyo round of multilateral trade negotiations, EEC and the U.S. are in the middle of an eight-year staged reduction in chemical tariffs. Accordingly, both EEC's statutory duty and the surcharge on U.S. methanol and vinyl acetate shipments will decline through 1987.

EEC is an important market for both products. In 1982, U.S. companies shipped $32.3 million worth of methanol to EEC countries, 36.2% of total methanol exports. U.S. vinyl acetate exports to EEC countries amounted to $32.7 million, or 21.5% of the total.

Rather than increase tariffs, EEC will slap quotas on U.S. shipments of styrene and certain grades of polyethylene sheet. The styrene quota is 25.6 million ECU (European currency unit). Early reports mistakenly listed the styrene quota at $25.6 million. But the exchange rate between the ECU and the dollar is constantly changing. Last year's average was about 90 cents per ECU. The current rate is about 81 cents per ECU.

An EEC spokesman says that the quota was listed in terms of the ECU because of the uncertain exchange rate. It would have been simpler, however, if the quota had been set by volume, rather than by value, she adds.

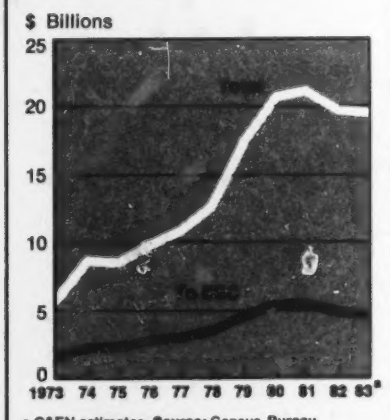
The quota on polyethylene sheet varies, depending upon thickness and density. The total value of the quota on three grades of sheet, however, amounts to 13.6 million ECU.

Before the EEC product list became official, rumor indicated that quotas would be imposed on low-density and high-density polyethylene resin (a much larger category) rather than on polyethylene sheet. Had this been true, the outcry from the U.S. chemical industry would have been far louder than it has been.

Considering past heated trade battles between the U.S. and EEC over chemicals, the reaction of U.S. chemical industry trade experts has been quite subdued. Most of them think that the EEC retaliation against chemicals is unfair. They feel that the U.S. chemical industry is paying the price for the steel industry's protection.

However, other than relay those feelings to the USTR office, there is

One fourth of U.S. chemical exports go to EEC



a C&EN estimates. Source: Census Bureau

EEC retaliation hits U.S. chemical exports two ways

Higher duties on methanol and vinyl acetate . . .

	Statutory duty, %	New surcharge, %	Resulting new duty, %
Methanol			
1984	13.5%	6.4%	19.9%
1985	13.4	5.1	18.5
1986	13.2	3.9	17.1
1987	13.0	2.7	15.7
Vinyl acetate			
1984	13.2	6.4	19.6
1985	12.6	5.1	17.7
1986	12.1	3.9	16.0
1987	11.5	2.7	14.2

. . . and quotas on styrene and polyethylene sheet

	Quota (million ECU[a])
Styrene	25.6
Polyethylene sheet	13.6
0.1 mm or less, density less than 0.94	9.1
0.1 mm or less, density 0.94 or more	2.0
More than 0.1 mm	2.5

Note: Effective March 1, 1984. a European currency units. Currently, 1 ECU = about 81 cents; 1983 average was 1 ECU = about 90 cents. Source: European Economic Community

very little that they can do about it. The Chemical Manufacturers Association is contacting chemical companies to determine the full impact of EEC's tariff and quota moves. It will pass these data along to USTR, which, hopefully, can put them to good use in continuing negotations with EEC trade officials.

There is still the possibility that the U.S. and EEC can reach agreement on a trade compensation deal before EEC's retaliatory moves become effective on March 1. Presumably, the two sides were close to an agreement before the tariff and quota action was announced. And some chemical trade experts see this action as an EEC attempt to prod U.S. officials into offering a satisfactory package of compensation.

Others believe that it is all but impossible for the two sides to reach agreement before the March 1 deadline. And they speculate that, if the U.S. decides to counterretaliate, a full-scale trade war between the two blocs could erupt.

It seems unlikely that negotiators on either side will allow this to happen. The present disagreement involves only about $160 million in trade. That includes not only the proposed EEC tariffs and quotas on chemicals, but similar restrictions on some sporting goods and burglar alarms.

Compared to this small value of U.S. steel restrictions and EEC retaliatory steps, total U.S.-EEC trade is huge. U.S. exports to EEC countries were $48 billion in 1982. Imports were $43 billion. □

Monsanto to acquire Belgian drug firm

Monsanto's fledgling health care business may have its first commercial products if a deal goes through for it to acquire Continental Pharma, a Belgian pharmaceutical company.

Continental Pharma is a privately owned company with sales in 1983 of about $40 million. It employs about 570 people at offices, three manufacturing plants, and a research center in Belgium. It produces ethical pharmaceuticals, which it markets primarily in Belgium and through licenses in other parts of the world. Continental Pharma's largest product, which it invented and markets, is Suloctidil, used to enhance peripheral and cerebral blood circulation. It is being studied in the U.S. for treatment of senility.

Monsanto, which expects to complete the acquisition by May, set up its health care division early last year, but so far has had no sales. The division was established to develop market strategy and has functioned essentially as a venture capital operation to provide funds to such biotechnology companies as Biogen and Collogen and to fund Monsanto's research grants to universities such as Washington University and Oxford.

Richard J. Mahoney, Monsanto's president and chief executive officer, says the planned acquisition is "an important step in plans to develop growth opportunities for Monsanto in health care products."

The Belgian company's research base would be expected to accelerate Monsanto's own R&D efforts in pharmaceuticals. □

Earl L. Muetterties dies at 56

Earl L. Muetterties, professor of chemistry at the University of California, Berkeley, and senior scientist at Lawrence Berkeley Laboratory, died Jan. 12 of cancer at his home in Oakland, Calif. He was 56.

A major figure in the world of inorganic chemistry, Muetterties made significant contributions to the fields of nuclear magnetic resonance, boron chemistry, organometallic chemistry, and surface science. He wrote more than 300 papers for scientific journals and was the inventor or coinventor responsible for about 100 U.S. and foreign patents.

"Many in research are productive in the sense that they add to the descriptive matter of the field of chemistry; and Muetterties has to his credit a large number of papers, carefully describing experimental work carefully done, which have expanded our knowledge of

Earl L. Muetterties

chemical systems," a colleague says. "Much rarer are the individuals who make contributions so basic and so significant that they transform a research area. Muetterties has done this in two major areas of inorganic chemistry: boron compounds and the stereochemistry of nonrigid species."

For the past several years, Muetterties' work has examined homogeneous catalysis by transition metal complexes. "Though many have referred to the opportunities in the field, Muetterties is the leader in changing potential to reality," the colleague says.

Muetterties began his scientific career at Du Pont's central research department in 1952 and was associate director of research there from 1965 to 1973. He was a professor of chemistry at Cornell University from 1973 to 1978 when he joined the faculty at Berkeley. He is survived by his wife, JoAnn, and six children. □

Reproductive hazards in workplace probed

A comprehensive examination of the issue of reproductive hazards in the workplace is being undertaken by the Office of Technology Assessment. The project, formally approved by OTA's board last fall, got under way last week with the first meeting of the project's advisory panel.

Reinforced Plastics Recovery Seen for 1984

After pulling a surprising upturn out of what started for the economy as a dismal 1983, reinforced plastics producers are saying that 1984 will be even better. In fact, they say, demand for reinforced plastics in 1984 will exceed the glory years of 1978 and 1979 when demand for reinforced plastics hit its all-time peak.

At this time last year producers were saying that demand for reinforced plastics would rise about 8.4% in 1983 from 1982 levels. They got this and more, as shipments rose almost 26% from 1982. Now they are saying that shipments in 1984 will rise a little more than 12%. That would put shipments of reinforced plastics at 2.16 billion lb, compared with 1.92 billion lb in 1983 and 1.53 billion in 1982. More important, it would finally push demand for reinforced plastics above the all-time high levels of 2.06 billion lb and 2.01 billion lb in 1979 and 1978, respectively, the last good years for reinforced plastics.

For the past five years, use of reinforced plastics, in effect, has not grown. The average annual increase between 1979 and 1984 is forecast at just 0.9%. And there have been actual declines in four markets—land transportation, marine, electrical, and appliances.

Between 1974 and 1984, reinforced plastics use will have grown at an average annual rate of 4.9%. Even here, however, demand in two of the end markets—marine and aircraft—will have declined a slight 0.3% per year from a decade ago.

These forecasts were reported last week to the annual meeting of the Reinforced Plastics/Composites Institute of the Society of the Plastics Industry in Houston. They are part of the yearly survey of producers and others in the industry prepared by Laura Morrison of the New York City-based public relations firm of Morrison/Gottlieb.

The leading gainer among the major reinforced plastics markets in 1983 was consumer goods, where demand increased more than 52% from 1982 to 128 million lb. Demand for reinforced plastics in consumer goods this year is expected to be up another 12% to 143 million lb.

Related to consumer goods, appliances were the second largest market in terms of growth last year. Here demand for reinforced plastics increased about 29% to 106 million lb. For 1984, demand for reinforced plastics in appliances is expected to climb another 16% to 123 million lb.

Demand for reinforced plastics in construction last year increased 28% from 1982 to reach 400 million lb. However, producers see this growth rate slowing considerably this year as they forecast demand in construction end markets to grow only 5.5% to 422 million lb.

Land transportation, the largest market for reinforced plastics, grew almost 28% to 458 million lb, thanks in no small part to the good automobile year enjoyed by Detroit in 1983. Producers expect that 1984 growth will be at a slower but still very good rate of nearly 18%, with demand topping 500 million lb for the first time since 1979, finally coming in at about 540 million lb.

The survey shows that of reinforced plastics shipped last year, 15%, or 299 million lb, were thermoplastics. This is forecast to increase about 9% this year to 326 million lb. However, it will slow slightly as a percentage of total product shipped, still accounting for about 15% in 1984.

Four markets accounted for most of the thermoplastic demand last year. About 155 million lb went to land transportation, 55 million to appliances, 49 million to electrical uses, and 16.5 million to consumer goods. These totaled about 276 million lb, or 92% of total reinforced thermoplastics. □

Reinforced plastics demand forecast to grow 12% in 1984 to beat previous highs

								% change		Average annual change	
Millions of lb	1984[a]	1983[a]	1982	1981	1980	1979	1974	1983–84[a]	1982–83[a]	1979–84[a]	1974–84[a]
Transportation, land	540	458	359	445	416	550	293	17.9%	27.6%	−0.4%	6.3%
Marine	309	276	230	290	275	385	320	12.0	20.0	−4.3	−0.3
Construction	422	400	312	309	287	335	198	5.5	28.2	4.7	7.9
Anticorrosion	320	288	235	275	252	238	174	11.1	22.6	6.1	6.3
Electrical	189	170	140	178	162	190	94	11.2	21.4	−0.1	7.2
Appliance	123	106	82	112	104	130	82	16.0	29.3	−1.1	4.1
Consumer goods	143	128	84	110	103	126	75	11.7	52.4	2.6	6.7
Aircraft	29	25	22	28	25	23	30	16.0	13.6	4.7	−0.3
Other	80	72	64	74	70	79	75	11.1	12.5	0.3	0.6
TOTAL	2155	1923	1528	1821	1694	2056	1341	12.1%	25.9%	0.9%	4.9%

a Estimate. Source: SPI Reinforced Plastics/Composites Institute

Future for metal-coated plastics is bright

U.S. consumption of metal-plated and metal-coated plastics will double during this decade to 190 million lb in 1990 from 1980's figure of 95 million lb, according to a study by consultants Margolis Marketing & Research of New York City.

Although automotive uses still will lead in use of these materials, electrical and electronic devices will show phenomenal growth, rising to almost a quarter of the market at the end of the decade. Company president James Margolis ascribes strength in electrical and electronic applications to Federal Communications Commission requirements for shielding of devices against electromagnetic and radiofrequency interference (EMI and RFI).

Whereas electroless plating and electroplating will remain the dominant processes, Margolis predicts that newer technologies will show larger increases, to be used for more than 25% of metal-coated plastics by 1990. He justifies this forecast by citing improvements in equipment, materials, and methods, as well as continuing regulatory strictures against effluents from traditional plating.

Also, ABS (acrylonitrile-butadiene-styrene) resins will continue to be the dominant substrates, but polyphenylene oxide-polystyrene alloys promise greatest increases during the period. Margolis says that new grades of such resins together with recent development of ultraviolet-cured top and base coatings will fuel the strong advance in these materials. Also, the presently minute markets of such other engineering resins as polyphenylene sulfide and polyethersulfone will show important growth for applications that combine reflectivity with high use temperatures, strength, flame retardance, and electric field resistance.

Growth in metal-plated and metal-coated plastics for automotive uses will increase 4% yearly to 65 million lb in 1990 from 44 million lb in 1980, Margolis says. Although the automotive segment is the slowest-growing market, this amount will be 35% of total U.S. consumption of these materials. By contrast, EMI shielding needs will trigger an increase from 4 million lb in 1980 to 23 million lb in 1985 and 45 million lb in 1990, for an overall average annual growth rate of 27%.

Zinc arc spray is the technique currently most in use for EMI, though Margolis expects electroless plating to be favored in the immediate future. This is because there is a large amount of plating capacity available, and performance of plated plastics is familiar to those in the industry. Arc spray uses an electric arc between two wires to melt the metal, which is sprayed onto the substrate by a current of air. Margolis says that changes are needed in vacuum metallizing equipment before that technique can find much use in EMI, but these improvements are on the way. Effective shield coating by this method requires a three-layer, chromium-copper-chromium treatment.

Other metal coating processes that will grow in importance this decade are sputter coating and hot stamping, Margolis says. In sputter coating, a beam of cations dislodges metal atoms from a negatively charged target, and these metal atoms coat the substrate. Margolis is especially optimistic about a variation in which a magnetic field focuses metal atoms more efficiently onto the substrate. In hot stamping, heat causes attachment of adhesive-coated metal foil to the substrate, followed by peeling away of a polyester film carrier layer. Hot stamping is favored for high-gloss and/or textured decorative metal coating and for solvent, detergent, or abrasion resistance. □

U.S. use of metal-plated and coated plastics will grow at 7% per year in the 1980s . . .

Millions of lb	1970	1975	1980	1985	1990	Annual growth, % 1980–85	1985–90
ABS[a]	19	43	53	81	92	8.8%	2.6%
Polypropylene	6	7	10	12	17	3.7	7.2
Polyphenylene oxide	2	4	6	15	25	20.0	10.8
Polyester[b]	10	12	14	17	20	4.0	3.3
Polyvinyl chloride[b]	0	4	4	5	6	4.6	3.7
Other[c]	3	5	8	12	30	4.1	20.1
TOTAL	40	75	90	142	190	8.4%	6.0%

. . . with fastest increases in electrical and electronics applications . . .

Automotive	18	36	44	57	65	5.3	2.7
Appliance	14	21	26	31	40	3.6	5.2
Marine & plumbing	5	12	15	21	28	7.0	5.9
Electrical & electronic[d]	1	2	4	23	45	42.0	14.4
Household products	1	2	3	5	7	10.8	7.0
Other	1	2	3	5	5	10.8	0.0

. . . but with electroplating and electroless plating lagging in growth

Chrome plating	38	70	85	120	140	7.1	3.1
Other[e]	2	5	10	22	50	17.1	17.8

a Acrylonitrile-butadiene-styrene. b Film. c Acetal, acrylic, cellulose acetate, epoxy, nylon, polycarbonate, polyphenylene sulfide, polysulfone, polystyrene, and polyurethane. d Includes electromagnetic and radiofrequency interference shielding and includes products that could be listed under automotive and appliance as well as computer and video game categories. e Vacuum metalizing, sputter coating, hot stamping, zinc arc spraying, flame spraying, and spray-applied nickel-polyurethane and nickel-acrylic coatings. **Source:** Margolis Marketing & Research Co.

Brisk Detergent Activity Changes Picture For Chemical Suppliers

Patricia L. Layman, C&EN London

For a mature industry, the soap and detergent business is showing a remarkable amount of activity. Some European researchers even claim that more has been happening in the industry in the past five years than in the 20 years before that. Although development may not be quite so frenetic in the U.S., the overall picture is clear: The industry is active because it is changing, and the changes—with the reformulations resulting—mean new opportunity for raw material suppliers.

The soap and detergent industry is vast. World production this year may hit an estimated 24.36 million metric tons. That includes household and toilet soaps, and synthetic- and soap-based laundry detergents, but omits such specialties as fabric softeners and many industrial detergents.

In industrialized countries, growth has been slow over the past few years. At one time, growth was linked to gross national product, but lately population growth is probably a more accurate indicator. At one time, the industry was considered recessionproof—people had to wash their clothes, didn't they?—but with the latest economic problems, that myth has been exploded, particularly in developing countries. All of which is to say that, overall, the industry has not been going through especially good times.

Why, then, all the new activity? It is a reflection, basically, of several trends that have swept the industry along. Some had happened earlier in the U.S. and are happening now in Europe and other regions, whereas others have been more universal. Europe now, for example, is refor-

Glossary of soap and detergent terms

Actives. In a detergent, the surfactants that provide the cleaning action. Actives can be soap, or synthetic detergents, or a combination of the two.

Amphoteric surfactant. A surfactant that may be either anionic or cationic in water, depending upon pH. Frequently used in shampoos and other personal-care products because of mildness.

Anionic surfactant. A surfactant with a negatively charged anion incorporated into the molecule. Tends to be high-sudsing. Major anionics are linear alkyl-sulfonates.

Antiredeposition agent. More accurately, antisoil redeposition agent, an additive used to help prevent soil from resettling on fabric after it has been removed during washing. Sodium carboxymethylcellulose is the classic "antiredep" agent, but increasingly, more sophisticated cellulose derivatives and synthetic polymers are used.

Biodegradability. For the detergent industry, a measure of a surfactant's ability to decompose by biological processes, especially by bacteria present in waste-treatment systems, in surface waters, and in the soil.

Bleach. A material that whitens, removes stains, and brightens fabrics. Can be formulated into detergents or used as a separate product.

Builder. A material that improves the cleaning efficiency of a surfactant, principally by inactivating water-hardness ions. Can function as chelating and sequestering agent, as precipitating agent, or as ion exchanger. Used in virtually all home laundry powders and in many home laundry liquids for heavy-duty cleaning. Detergents formulated with builders are termed "built."

Cationic surfactant. A surfactant with a positively charged ionic group in the molecule. Not generally used for cleaning per se, rather for disinfectant-cleaners, and in fabric softeners. Quaternary ammonium compounds are most commonly used cationics.

Corrosion inhibitor. A material that protects against abrasion and corrosion of appliance surfaces, and protects china and metal washed in automatic dishwashers. Sodium silicate is the most commonly used corrosion inhibitor.

Enzymes. In the detergent industry, the amylase and protease enzymes used to catalyze biological decomposition of proteinaceous stains on fabrics, so the stains then can be removed by surfactants.

Eutrophication. The complex process of nutrification of a body of water. Nutrients from a variety of sources nourish algae in the water, causing them to flourish and eventually swamp the oxygen in the water otherwise available to decompose dead organisms. The result is, eventually, a sludgy, silting-up body of water. Necessary nutrients are nitrogen, potassium, and phosphorus; because detergent phosphates come from a highly identifiable and isolatable source, they frequently have been singled out as a major culprit in eutrophication. Hence the pressure for their banning in areas troubled with eutrophication.

Fatty alcohols. The primary alcohols of C_6 to C_{22}, usually straight chain, which are an intermediate for nonionic surfactants in particular. Historically derived from natural sources such as tallow and coconut oil; more recently primarily produced, by several different routes, from petrochemical raw materials.

Foam booster. An additive to boost suds production and stabilize lather. Alkanolamides are the most frequently used foam boosters.

Foam depresser. An additive to suppress or inhibit the production of suds or control suds at a low level. Soap, as part of a surfactant system, helps control foaming; silicone compounds, used at very low levels, are also effective foam depressers.

"Hard" surfactant. A surfactant difficult, or hard, to decompose biologically—that is, of low biodegradability. Branched-chain surfactants, in particular branched-chain alkylbenzene sulfonates, tend to be "hard," and came under fire in the early 1960s as contributors to foam in the waterways. Use in detergents was given up voluntarily by producers at that time in North America and Western Europe.

Heavy-duty detergent. Generally a built detergent, designed for cleaning the total family laundry, including heavily soiled items.

Light-duty detergent. Generally an unbuilt detergent designed for light cleaning tasks, such as hand dishwashing or fine-fabric washing.

Liquid hand soaps. Toilet soaps formulated as liquids rather than a bar. The term tends to be a misnomer, because, by and large, the formulations are based on synthetic detergents, although some products have been put together around potassium soaps.

Nonionic surfactant. A surfactant containing neither anionic nor cationic functional groups. Tends to be low-sudsing. Ethoxylated alcohols are the most widely used nonionics.

Saponification. The process of converting a fat, such as tallow, into a soap by treating it with an alkali such as sodium hydroxide. Yield is soap and coproduct glycerin.

Soap. Reaction product of saponification. A mildly alkaline surfactant which, unfortunately, tends to interact with water-hardness ions, forming insoluble soap curd which precipitates out onto fabrics and appliances. Though not a problem in soft-water areas, soap-curd occurrence spurred the development of synthetic detergents, which are less affected by water hardness.

"Soft" surfactant. A surfactant that is relatively easy to biodegrade, thus the opposite of "hard" surfactant. Generally these are linear molecules, such as linear alkylsulfonates (LAS). Sodium dodecylbenzene sulfonate is the major compound within the LAS family of surfactants.

Surfactant. The common contraction for surface-active agent, referring to an organic compound that changes the properties of the surface of the liquid to which it is added. Detergent surfactants (and soap, which is also a surfactant) lower water's surface tension, enabling faster wetting of a fabric being washed. Soil can then be more readily loosened and removed.

Source: Soap & Detergent Association

Cooler water used in increasing percentage of washloads

Note: Hot = 127 °F, warm = 95 °F, and cool = 63 °F.
Source: C. A. Houston & Associates

mulating detergents to cope with lowered washing temperatures and the increasing share of the washload held by synthetic-fiber textiles, while handling the heavier soil loads commonly found with European washes.

More widespread has been the need to reformulate, or at least re-evaluate, builder systems, as actions against phosphates continue in Europe and are rekindling in the U.S. after nearly a decade of calm.

And with the reformulations, the soap and detergent industry offers yet another example, that in new directions, it is the smaller company that takes the chances and makes the new-product introductions.

Given an industry as vast as soap and detergents, it probably is not surprising that it tends to be dominated on a world scale by a handful of companies. Looking strictly at soap and detergent sales, at the top of the pile is Procter & Gamble of Cincinnati. London-based Unilever is second. New York City-based Colgate-Palmolive is third, and Henkel of Düsseldorf, West Germany, is fourth.

Unlike the U.S. market, however, where P&G, Colgate, Lever, and the U.S. fourth, Purex Industries, totally dominate the business, on a worldwide basis, the international Big Four have less than half the market. The remaining share—about 53 to 55%, is split among innumerable small, local, or regional producers. In Europe, for example, the Association Internationale de la Savonnerie et de la Détergence, an association of European national associations in the industry, estimates that its member groups represent more than 700 detergent and soap makers.

Moreover, on a worldwide basis, the Big Four generally tend to do most of their business close to home. P&G's total sales, for example, are about 70% in the U.S. Unilever's are about 65% in Europe, and Henkel does about 80% of its business in Europe. Only Colgate has less than half its sales at home: about 40% in the U.S., and the rest split almost equally between Europe and the rest of the world.

The situation is somewhat different with raw material suppliers. There are a few small local or regional suppliers, but basically major national or multinational companies supply most detergent active ingredients, or formulating products such as builders, bleaches, and fillers. The major detergent producers provide such a large demand, suppliers have to be large to produce enough material to supply their big customers. Some companies have divisions to concentrate strictly on this market. BASF, for example, has just restructured some of its operations into a specialty chemicals—for example, detergents—division.

And because most of the active components in modern detergents are petrochemical-based, suppliers have brought along the economies of scale that always have accompanied basic petrochemical production.

Perhaps the trend having the most profound impact now on the soap and detergent industry worldwide is a move toward lower washing temperatures. This trend has been taking hold for a number of years in the U.S., of course, particularly as energy-conscious consumers seek to trim electricity bills for heating water.

But in the U.S., "hot" has always been a relative term: probably about 50 to 60 °C. In Europe and many other areas of the world, "hot" is 90 to 95 °C, often referred to as "at the boil." Bleaching systems were formulated originally for optimum performance at these temperatures, and the white cottons and linens used then came out sparkling clean. Energy-consciousness has hit the European consumer hard, however, and both detergent makers and washing-machine producers have been working to design systems that will do the bulk of a family's washload at 60 °C, with an increasing option of doing some of the wash at an even lower temperature, usually about 40 °C.

In that, the industry is approaching the level of that in Japan, where the usual laundry temperature is 30 °C or below. In Mexico, an even more extreme example, historically laundry has been done in cold water.

Temperatures as low as that pose challenges for detergent formulators whose palette up to now has been filled with materials that perform best in warmer water. Formulators have to make sure the active will dissolve readily in cold water—one commonly used surfactant in the U.S., for example, tallow alcohol sulfate, tends not to dissolve well in cold water. They must ensure that the bleach system will perform efficiently—perborate bleaches must have boosters or activators when put in products destined for cool- to warm-water washing, else lose much of their efficiency. They have to make sure the foam generated will be sufficient to assure the consumer that the detergent is working hard, but not so much that it overflows or clogs up a system.

Most detergents on the market are still aimed at the warm wash, although many packages, especially in the U.S., do note that the products are suited for cold-water washing. And Lever, of course, sells cold-water All in the U.S.

In Europe, cold-water washing per se is generally looked at askance. Out to prove that it can be a good market

segment, however, is a small British manufacturer, Stridebond, of Newcastle-Upon-Tyne, which last summer introduced a cold-water liquid. The company decided upon liquids, after concluding that the powder-detergent market would be too difficult to break into, and built a plant capable of turning out 17 million lb per year of liquid detergent. The product works at temperatures up to about 60 °C, the company says, but its promotions are aimed at cold water—just above freezing, if need be, with the cool water saving both on energy and fabric wear-and-tear.

How successful Stridebond is with its Cold Force remains to be seen, of course. Some industry observers question the wisdom of going to a liquid formulation. Heavy-duty liquids have been quite popular in the U.S. detergent market, capturing just under 20%. But they have remained at that 20% for a while, and earlier predictions of 25 or 30% of the market were clearly too optimistic. And they have met with mixed reaction in Europe, where they probably hold no more than 8% of the heavy-duty detergent market, in value, and 5% in volume.

In France, liquids have been the consumers' darling, and now hold more than 10% of the market. But elsewhere, the picture is different. In the Netherlands, liquids' share of market is closer to about 4% and falling, in West Germany about 8%, and in Switzerland about 4%.

European researchers contend that the liquids simply are not so effective as heavy-duty powders, and that whereas the difference in performance might not be so noticeable on the lighter soils and lower wash temperatures of the U.S., they are decidedly noticeable under European washing conditions.

One area in which U.S. detergent formulations are moving closer to those in Europe and Japan is in the use of enzymes. These materials had found significant popularity in the U.S. and Europe during the 1960s, because of their ability to tackle proteinaceous and carbohydrate stains on laundry. Either as presoaks or formulated into laundry detergents, the materials could tackle and enzymically decompose for further cleaning such stains as blood, egg, gravy, and the like.

But then reports of skin and respiratory problems among production workers popped up. There were never any charges that the consumer would be harmed. Rather, the problem was with workers in detergent factories who inhaled the dust. The enzymes then used were very small particles, easily dustborne, and some of them, proteases, could attack the respiratory tissue. Consumer activists jumped on the issue and began campaigning against enzymes, government agencies began to worry about their use, and in early 1971 enzymes were pulled out of formulations. The detergent market for them collapsed.

Later that year, however, the U.S. National Academy of Sciences concluded that the average enzyme-containing detergent produced no more skin irritation than ordinary laundry products. Moreover, enzyme makers had developed new production methods to turn out enzymes that were low-dust, coated granules. That innovation resolved the problem of worker respiration.

In Europe, enzymes promptly were reincorporated into detergents, and now probably two thirds of all premium-quality heavy-duty detergents there contain enzymes. Japan's detergent makers reformulated all

Detergent formulations around the world have great variety

% of total formulation	Heavy-duty powders, U.S., Canada, Australia	Heavy-duty powders, South America, Middle East, Africa	Heavy-duty powders, Europe	Heavy-duty powders, Japan	Heavy-duty liquids	Light-duty powders (primarily Europe)	Light-duty liquids	Detergent laundry bars
Actives[a]	6–20%	17–32%	8–18%	19–23%	15–50%[b]	14–25%	15–37%	18–30%
Foam boosters[c]	0–2	—	0–3	—	0–4	—	0–5	—
Foam depressants[d]	—	—	0.3–5	1–2	—	—	—	—
Builders[e]								
Sodium tripolyphosphate	25–35	20–30	20–35	0–15	10–30	10–40	—	—
Mixed or nonphosphate	15–30	25–30	20–45	0–20	15–20	—	—	25–45
Sodium carbonate	0–50	0–60	—	—	—	—	—	15–30
Antiredeposition agents[f]	0.1–0.9	0.2–1	0.4–1.5	—	0–2	0–0.9	—	0.3–2.0
Anticorrosion agents[g]	5–10	5–12	5–9	15	2–5	0–8	—	3–8
Optical brighteners	0.1–0.75	0.08–0.5	0.1–0.75	—	0.1–0.5	0–0.3	—	0.05–0.3
Bleach[h]	i	—	15–30	—	—	—	—	—
Enzymes[j]	i	—	0–0.75	—	0–1	—	—	—
Moisture	6–20	6–13	4–20	—	Balance	6–14	Balance	3–14
Fillers[k]	20–45	10–35	5–45	—	—	15–45	—	See sodium carbonate
Other ingredients[l]	—	—	—	—	—	—	6–9[m]	15–20[n]

a Mostly alkylsulfonates (linear and branched), fatty alcohol ethoxylates, and fatty alcohol sulfates. b Includes up to 10% soap in European formulations. c Ethanolamides, such as cocomonoethanolamide. d In small levels, silicones; at higher levels, soap. e Some formulations use only sodium tripolyphosphate; others have mixtures of tripoly with other phosphates (for example, sodium orthophosphate), aluminosilicate zeolites, the sodium salt of nitrilotriacetic acid, sodium citrate, and sodium carbonate; still others use the other builders alone or in various combinations. f Sodium carboxymethylcellulose, other cellulose-based polymers, or synthetic polymers. g Sodium silicates (as purchased solutions). h In U.S., sodium perborate, when used. In Europe, formulations for high-temperature washing have sodium perborate, whereas those for use at lower temperatures include boosters such as tetraacetylethylenediamine. i A few formulations include 20 to 25% bleach and up to 0.75% enzymes. j As purchased granules. k Predominantly sodium sulfate. l Usually also include small amounts of coloring agents, opacifiers if desired, fragrance, etc. m Primarily viscosity builders. n Predominantly sodium bicarbonate, but can also include other filler materials such as kaolin and talc.

Detergent intermediates capacity far outstrips demand

Linear alkylate capacity (thousands of metric tons)

U.S. producers		Western Europe producers	
Vista (Conoco)	170	Shell	175
Monsanto	109	Petresa	150
Witco	20	Chimica Augusta	140
		Hüls	80
		Montedison	35
		BASF	30
		Texaco	25
Total nameplate	299[a]	Total nameplate	635
Effective	272	Effective	515
Demand	240	Demand	325

Fatty alcohols capacity (thousands of metric tons)

U.S. producers		Western Europe producers	
Shell	210	Henkel	120
Ethyl	108	Shell	60
Vista (Conoco)	106	Condea	60
Procter & Gamble	98	BASF	12
Sherex	9	ICI	12
Celanese[b]	23	PCUK	8
		Chimica Augusta[c]	50
Total nameplate	554	Total nameplate	322
Effective	390	Effective	305
Demand	210	Demand	160

a Union Carbide closed down its 73,000 metric tons of capacity in 1983. b Retrofitted plant to be opened. c Rumored to be reopening plant now closed.

their major brands in about 1978 to include enzymes.

Progress toward their use in the U.S. has been slower, mostly because the term "enzyme" became such an emotionally traumatic one for the consumer. But detergent makers are putting them back into products, and enzyme makers have high hopes for the market. For example, one of the major enzyme makers, Gist Brocades of the Netherlands, several years ago put together a share issue to construct a new detergent enzymes unit at its Kingstree, S.C., plant. The company said at the time that U.S. demand for detergent enzymes eventually would far outstrip that of Europe.

One estimate holds that present sales of detergent enzymes make up 15% of total enzymes sales in the U.S., as detergent makers put them back into products. Contrary to several decades ago, there is little fanfare marking their reintroduction. And gone is the once-magical word "enzymes." Now a snappier, more specific "protease" or "amylase" does nicely for the detergent maker trying to put together a superior product.

If enzymes are still a controversial subject in the U.S., antisoil redeposition agents—better known as antiredep agents—are not. And researchers are finding this field a fertile one. The classic antiredep agent has been, and continues to be, sodium carboxymethylcellulose. But as with most of the classical detergent components, it was developed to perform on cottons and other cellulosics. Suppliers such as BASF and Rohm & Haas contend that this compound is less efficient in preventing soil redeposition on synthetics and blends. Their suggestion instead: polyacrylic acids and polyacrylates, from 1 to 6% in a formulation.

However, with the carboxylic acid group present, offering the potential to sequester troublesome water-hardness ions, producers of the polyacrylates see a possible market as a builder. After all, sodium citrate already functions as a sequestering builder in Lever Brothers' Wisk liquid detergent in the U.S. Polyacrylates probably would not be used as a sole builder, but as a cobuilder with other builder materials—with low-phosphate formulations, for instance, as the environmentalist campaigns against phosphates are rekindled in some areas in the U.S., and as phosphate limits are tightened in some European countries.

The most frequently used phosphate builder is sodium tripolyphosphate. Not only is it an excellent sequestering agent, but it helps during the manufacturing process. Because it forms a stable hydrate, it allows the product to contain relatively high amounts of moisture without sticking in the equipment. And because it has been used for so long, detergent manufacturers have essentially worked its cost into the selling price of laundry powders. Its cost-efficiency becomes the standard which other products must match or better.

The height of the controversy over phosphates in detergents in the U.S. came in the early 1970s. At that time, most of the localities in which there was perceived to be a problem with eutrophication of the waters passed their laws. Some banned phosphates altogether, either in automatic dishwashing detergents or in laundry detergents. Some states or localities set limits on the amounts of phosphorus that could be used.

Similarly, although at a somewhat later time, European countries that also perceived a problem with eutrophication of their waters put out limiting legislation. Most of the legislation put a phased reduction into effect. For example, in West Germany, sodium tripolyphosphate made up about 40% of a typical detergent formulation—10% phosphorus—in 1975, before the legislated limits went into effect. That was the equivalent of 270,000 metric tons per year of demand for tripolyphosphate. When the first stage of the reduction went into effect, the typical average dropped to 30% tripolyphosphate (7.5% phosphorus), or about 160,000 metric tons per year. The second phase went into effect Jan. 1 this year, and the average will drop to 20 to 24% tripolyphosphate (5 to 6% phosphorus), or about 120,000 metric tons per year of demand.

With those kinds of limits, or with the threat of phosphate bans increasing in number in the U.S., detergent makers are being forced to consider at least cobuilders to retain the cleaning efficiency of their brands, or are attempting to switch away from phosphates completely.

One of the first to switch away completely in the U.S. was Desoto

The heat once again is on phosphates

After a period of relative quiet, detergent formulators are facing an upswing in action against phosphate builders, both in the U.S. and elsewhere around the world. To some extent, it is a matter of beleaguered public officials seeking to attack what is still perceived to be a problem of eutrophication. It sometimes is also a matter of "politicking"—eager politicians courting popular approval by attacking an industry that is vast and very visible, even though such action may be unfounded.

In the U.S.: At the present, in the U.S., six states—Indiana, Michigan, Minnesota, New York, Vermont, and Wisconsin—ban the use of phosphates in home laundry detergents. And all six also limit the phosphate content, the equivalent of 8.7% phosphorus, in automatic dishwashing detergents.

Additionally, localities have their own bans. Dade County, Florida, which includes Miami, has a total ban, as do Chicago and many of its suburbs, and Akron, Ohio, and some of its suburbs.

Other areas have opted for limits. Connecticut, Florida, Maine, and about 15 municipalities limit phosphorus content to 8.7% in household laundry detergents. It will be limits, rather than a ban, in Maryland, if the new legislature starting up this month adopts a bill already filed with it to limit phosphates to a level to be set later on.

And in Ohio, two bills introduced in 1983 and scheduled to be carried over would prohibit the sale of household detergents containing more than 0.5% phosphorus. The ban would be effective for the 35 Ohio counties in the Lake Erie drainage basin.

In Canada: There is a federal limit on the use of phosphates in household detergents. The limit is set at 2.2% phosphorus.

In Europe: Phosphates vis-a-vis eutrophication is basically a regional, or national, issue rather than a pan-European issue suited for the European Economic Community; national or regional authorities have been responsible for tackling the problem in their own ways. Some countries, notably Sweden, have decided the best way to tackle water eutrophication is through tertiary sewage treatment systems. By the end of 1983, for example, Sweden had built more than 850 such treatment plants, and some 80% of the urban population of Sweden are connected to tertiary treatment systems. Most other countries that have a perceived problem, however, have turned to phosphate limitations.

For most countries, the limits set—and by and large, they are limits, not bans—are complex formulas dependent upon such factors as water hardness. For example, in West Germany, a decree has set the maximum amount of phosphates in detergents with scheduled reductions, in phases. The first reduction went into effect on Oct. 1, 1981, and the second stage began at the first of this year. A typical reduction: for water of 0 to 7 degrees German hardness (the equivalent of 0 to 126 grains in the U.S.)—that is, soft—a decrease from 0.7 to 0.5 g per L maximum phosphorus for home laundry detergents. Allowable limits are higher for harder-water areas. Rather than the solution being one of different formulations for different areas, however, there generally will be a standard formulation from each detergent maker, with a chart giving precise use rates for a washload in the various areas. The laundry-doer at home thus has the choice of supporting the limits, or of being a scofflaw.

In Italy, the government introduced a phosphates limit in March 1982, as part of a general law on the environment. And in the Netherlands, there has been a voluntary reduction in phosphate levels by the industry, in two stages. The latter stage went into effect Jan. 1, 1983.

Switzerland has perhaps the most severe problems with eutrophication, because of its geology. The country's legislators started in 1977 to determine legal limitations to phosphate content in detergents, and on Dec. 8, 1980, the federal government approved a two-stage reduction in limits. The first stage went into effect Oct. 1, 1981, and the second stage Jan. 1, 1983. But, again, the reductions were to a complex set of limitations, with a range of levels of phosphate allowed.

And in Norway, which also has special problems, particularly with its Lake Mjøsa, the industry and government worked out an agreement to limit phosphate content in household laundry detergents to 12% sodium tripolyphosphate. However, there is a total ban on the builders for automatic dishwashing detergents.

Phosphate reductions are currently under discussion in Austria, but no decisions have been reached. And in Finland, a gentleman's agreement between industry and government has limited phosphate content to the equivalent of 7% phosphorus.

In Australia: The topic of phosphate reduction is under discussion but there is some feeling that the problem is more political than actual.

In Japan: Although only some of Japan's prefectures have instituted bans on phosphate use, because of the country's marketing patterns, detergent makers decided upon total reformulations. As a result, within only two years, more than 90% of the detergents produced and sold in Japan are phosphate-free, built instead with zeolites.

Chemical, which makes all of Sears' laundry detergents. Desoto turned to using a sodium carbonate-built formulation in the early 1970s and has continued with that particular builder system.

Few other companies have followed Desoto's lead, however. Nor have many other manufacturers followed Lever Brothers, which reformulated its Wisk liquid detergent builder system from phosphates to sodium citrate.

A major builder to be tapped, either for use alone or with phosphates, has been the zeolite family. In Japan, for example, zeolites are the sole builder in more than 90% of all detergents sold.

Henkel has the patents nearly worldwide on zeolite builders, based on its technology for Sasil—sodium aluminosilicate—zeolites. It has licensed zeolite production to Degussa in West Germany and Italy, to Mira Lanza and Montedison in Italy, to Akzo and Zinkwit/Crosfield (a Unilever interest) in the Netherlands, and to PCUK/Rhône Poulenc in France, in Europe alone. As recently as August 1983, production capacity for detergent zeolites in Europe was at least 210,000 metric tons per year.

CIRCLE 15 ON READER SERVICE CARD ⟶

(That includes 65,000 metric tons capacity at Henkel, strictly for captive use.)

Henkel also has licensed production elsewhere in the world—in Japan, for example. In the U.S., the patent situation is somewhat murky. It is a rather sore subject with Henkel researchers—"We filed four weeks before Procter & Gamble," one says—that it had been unable to win the U.S. patents, too.

In the U.S., capacity is dominated by Ethyl Corp., whose zeolites plant at Pasadena, Tex., went on stream in the late 1970s with capacity of about 100,000 metric tons per year. And PQ Corp. put on stream in September 1982 its 30,000 metric-ton-per-year plant in Kansas City, Kan.

So with that kind of capacity, just what is being done with zeolites? In Japan, a lot. In Europe, toes are in the water. In the U.S., not much.

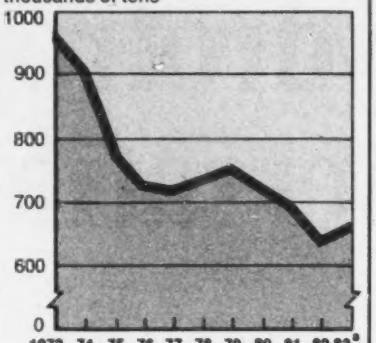
Zeolite-built formulations, either using zeolite as a cobuilder with phosphates or as sole builder, in Europe are basically being sold only where there are phosphate limits. There would be little likelihood of finding them, for example, in the U.K., because there is no eutrophication problem there, hence no phosphate limits.

For the phosphate limit areas of Switzerland and West Germany, however, detergent makers are trying zeolites. After a limited test market in Luzerne, Henkel brought out a phosphate-free detergent, Dixan, in both Switzerland and West Germany. But rather obviously, the company still regards the product as having to prove itself. There has been little if any promotion to the effect that the product has no phosphates in it. The only clue is absence of the term "phosphates" on the contents label.

That perhaps is one indication that detergent makers still really don't think zeolites are the ultimate answer. It is one thing to predict, on a theoretical level, that losing the "freedom to formulate detergents with any safe and effective ingredient . . . will prove counterproductive to the consumers' interest in value for money," as did the chairman of the European detergent association's technical commission recently. But it is another thing to watch that counterproductivity in action in the marketplace, as market share is lost for a product whose performance has slipped.

Top detergent phosphate in U.S. has suffered decline

Sodium tripolyphosphate production, thousands of tons



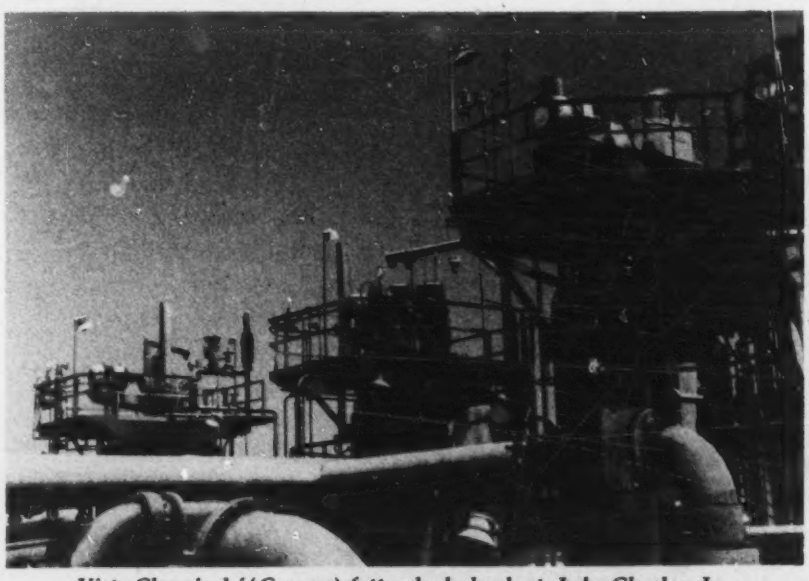
a C&EN estimate. **Source:** Commerce Department

Industry observers say that that is what led P&G to reformulate the zeolite-built products it had been marketing in phosphate-limit areas. Producers of zeolites in the U.S. had high hopes for P&G's success with the zeolite formulation. If P&G made it, the reasoning went, the market would quickly expand throughout the rest of the industry. P&G's reformulation, back to phosphates—to a level of 8.2% phosphorus, just under most of the limits of 8.7% phosphorus—dashed those hopes, and left some nearly new zeolite plants woefully underutilized.

On the other hand, P&G is continuing its limited test-marketing of sodium nitrilotriacetate (NTA) as a builder for detergents in Indiana, where phosphates are banned. It had been test-marketing detergents with NTA in New York state, another ban area, but backed off there in fear that the state would legislate a ban on NTA as well.

NTA has been tested and debated as a replacement builder since the early 1970s when the phosphate issue first arose. It is already in full use in Canada and in Finland. But because of early fears about carcinogenicity, or about heavy metals carried into the drinking water supply by superefficient sequestrant NTA, U.S. officials have never smiled on the material. The Environmental Protection Agency has said only that it sees no reason to ban the material, a statement far short of endorsement. However, the New York State Environment Commission has decided to look into the matter, and labor unions and consumer groups are still actively anti-NTA.

Consumers in Europe also tend to have a similar reaction to NTA, except in Finland. Perhaps for that politically powerful reason, most governments have advised caution over wholesale introduction of the builder as a replacement or an extender for tripolyphosphate.



Vista Chemicals' (Conoco) fatty alcohols plant, Lake Charles, La.

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The bleach dilemma: separate or united?

For the consumer, modern bleach systems are a vast improvement on the old standby of "lawn bleaching"—spreading laundry out on the ground to allow the sun to do the bleaching. But the washing habits of different countries have led to the development of two distinctly different philosophies of bleaching, one of adding bleach as a separate product, and the other of incorporating it into a laundry-detergent formulation.

For the U.S., the industry and consumers historically have tended to regard bleach as a separate item to be added along with the detergent, or used separately as a prelaundry soak.

In Europe, on the other hand, detergent makers have incorporated bleach into their formulations for many years. The German detergent maker Henkel's premier brand Persil, in fact, was a contraction of sodium perborate and sodium silicate, indicating the existence of bleach in the formulation when it originally was developed as a soap powder in 1907. (In 1909, the rights to the product and name were acquired for use in the U.K. by a company that subsequently became part of Unilever.)

Perborate as the bleach fit in nicely with European washing habits. The cottons and linens most common then could be put "to the boil," at 95 °C, at which temperature the perborate would be more than 90% effective as an oxygen bleach for wine stains and heavy soil stains. And even if lower temperatures were used, for the small percentage of the washload that was colored, the temperatures were still high enough that most of the perborate efficiency was retained. With that kind of formulation to depend upon, then, the consumer seldom needed special bleaching products, such as liquid chlorine. Chlorine, with its typical odor, came to be associated with disinfection, hospital cleaning, and other similar applications.

In the U.S., washing temperatures were never so high as those in Europe. More typically, "hot" was around 55 °C, and at such relatively low temperatures, perborate is only about 60% effective. Moreover, clothes and linens tended to be used for shorter periods of time before they were washed, so not all of them needed bleaching. Those factors encouraged the development of separate bleaches, for use only when an actual need was perceived. Several detergent brands are on the market in the U.S. with an oxygen bleach in the formulation—Oxydol, for example—but they aren't really typical.

In both the U.S. and Europe, the industry has been facing some problems with bleaching technology, for several different reasons. In the U.S., the rapid rise of synthetic fibers, which can be affected adversely by chlorine bleach, has given a boost to oxygen bleaches. Such products have been around for years, dry powders in the shadow of liquid chlorine bleaches.

And in Europe, a general drop in washing temperatures has meant a decrease in perborate bleach efficiency. Here, the answer has been the development of bleach activators, to help boost performance back to nearly the level of that "at the boil." Several boosters are being used in Europe: pentaacetyl glucose, frequently found in private-label brands, and tetraacetylethylenediamine (TAED). The TAED releases into solution the unstable peracetic acid, which becomes the bleaching agent at the lower temperatures.

Recycle unit at Interox's sodium percarbonate plant at Deer Park, Tex.—a U.S. beachhead

Oxygen bleaching in both the U.S. and in Europe has been the province of sodium perborate, and manufacturers of any other oxygen-bleach materials have had to struggle to gain acceptance.

A case in point is Interox, with its sodium percarbonate plant built in 1979 near Houston, and its other, specialty oxygen bleaches. Sodium percarbonate has been slowly gaining some use in Europe, in particular, but it may be in the specialty field that Interox has found a winner: with its magnesium monoperoxyphthalate hexahydrate. The material, which releases the peroxyacid anion in solution, has been adopted by Henkel for its new Fewa specialty detergent for delicate fabrics and hard-surface scouring cleansers. For products for use at higher laundry temperatures, however, European detergent makers are sticking solidly with perborate and TAED.

The West German government has probably come closest to tackling the issue. Last September, at the final meeting of the NTA Working Group, consisting of representatives of the Federal Ministry of the Interior and water supply authorities, among others, the group recommended an annual level of 25,000 metric tons of NTA be allowed in the environment. That would be equivalent to 3.4% NTA in a formulation. The group also recommended formulation of a monitoring program to measure the NTA in sewage, with a maximum limit of 0.2 mg per L.

A use level of 3.4% in a formulation would be too absurdly low to be effective, but as the number is an average, detergent makers could have more efficient levels in some formulations, and none in others.

The Netherlands also has set a maximum level on use of NTA—a 5% NTA average. But it also has set as its goal a total phosphates ban by 1987–88. As it stands now, there are no actual bans in Europe.

NTA producer BASF says that the monitoring program will be successful enough to encourage more widespread approval of the builder. Hence, its decision to start construction of a 36,000 metric-ton-per-year NTA plant in West Germany, to be finished by October 1984.

The evolution of surfactants continues after 40 years

The first synthetic detergents were introduced, in the 1930s, in areas where water hardness and mineral content were the highest, and the resulting soap curd problems the most severe. The surfactants were anionics—first, sulfated alcohols, and, later, sulfonated alkylbenzenes. As detergents continued to spread from hard-water areas to regions with softer water and less soap-curd occurrence, anionics consolidated this hold on the synthetic-detergent formulations.

The anionics had strong, rich lather, a characteristic that consumers already associated with cleaning efficacy. And they were, indeed, efficient cleaners of the fabrics found in the average wash-load—cottons, by and large. In 1950, for example, cottons accounted for more than 70% of the world's production of textile fibers, with synthetic fibers at about 18% and wool 10%.

By the early 1960s, however, detergent makers and intermediates suppliers had begun running into problems. First to hit the industry hard was the problem of biodegradability. The first generation of alkylbenzenes developed for sulfonation were branched chain, hard for microorganisms to break down in sewage disposal plants and in nature. Sewage treatment plants started seeing foam buildup as a result, and foam also began appearing in rivers and streams, and even from the household tap.

There was never a serious question of toxicity, just of the biodegradability of the materials. And in 1964, in the U.S., producers voluntarily agreed to switch their formulations to analogs of the branched-chain surfactants, linear alkylbenzene sulfonates. Similar actions took place in Western Europe at about the same time.

Anionics suppliers weathered that convulsive shift reasonably well. But the boom in synthetic fibers was another story. By 1964, synthetics had started serious growth, accounting for about 28% of the world's production of textile fibers. Cotton's share had begun shrinking, hitting about 62%. Seven years later, cotton was down to 50%, and synthetic fibers had jumped to 40%. Detergent makers decided that, as good as the anionics were at cleaning cottons, the nonionics were better at cleaning the synthetic fibers, and the rise in consumption of nonionics started to follow that of the new fibers.

Nonionics also got a boost—in the U.S., at least—from Shell's decision to build its 210,000 metric-ton-per-year detergent alcohols plant at Geismar, La., early in the 1970s. The plant, twice the size of any of Shell's competitors, helped lower the cost of nonionics—to a great extent, it still sets the price for the market—and the assured abundant supply and aggressive selling helped move the products into more general use.

Another plus was a better resistance to hard-water ions than the anionics, which helped them move into formulations when phosphate bans began hampering detergent efficacy. Since nonionics are easier to incorporate into liquid detergents than are anionic surfactants, they got a boost when liquid heavy-duty detergents began their dramatic rise in popularity in the mid- to late 1970s; from a 4% share of market in 1970 to now just less than 20% of the heavy-duty detergent market.

The 1980s, however, have brought a certain equilibrium to the industry. The shifts now will be horse-trading—a bit of a gain by nonionics at the expense of anionics, here; a bit of a gain by anionics at the expense of nonionics, there. In the developed countries, there is not that much growth these days to offer splendid growth opportunities for surfactants suppliers.

In the developing countries, on the other hand, there is still a strong growth, or a resumption of growth, after it was temporarily stifled by poor economic conditions. There is also a good deal of reformulation going on, as developing countries shift their production and consumption to biodegradable surfactants. Vista, for example, estimates that demand for branched-chain alkylbenzenes is still 456,000 metric tons per year, mostly in Latin America and the Far East. But even those markets are gradually eroding.

Although there is a global pricing pattern to the surfactant industry, little product actually travels back and forth, but rather is usually consumed close to where it is produced. One exception is branched-chain alkylates, for which the three major suppliers are Chevron, with a 130,000 metric-ton-per-year plant in Richmond, Calif., followed by Rhône Poulenc in France and Nippon Petrochemicals in Japan. Both of the two latter operations have some Chevron involvement. With that spread in geography, worldwide distribution is assured.

The other surfactants waiting for their time to come are those based on natural fatty alcohols. Such alcohols have been around for decades, of course, and long provided the only source of raw material for making detergent-range alcohols. But by 1970, the petrochemical products had started to make their inroads, and now naturals are only about a third of the business. Procter & Gamble, with its captive 98,000 metric-ton-per-year plant, and Henkel, with its estimated 170,000 metric-ton-per-year plant, both use natural feedstocks. Sherex uses naturals for its alcohols, and Condea in West Germany has about half its capacity suited for making alcohols from naturals.

There has been increasing interest in augmenting natural supplies in the past few years, although a variety of reasons has caused most such plans to be shelved. For example, Conoco Chemicals had completed an extensive engineering study for a natural-alcohol plant in the U.S. prior to its acquisition by Du Pont; that plan is now, at least for the time being, shelved at what has now become Vista Chemicals.

And Henkel had plans to build a plant with Union Carbide in the U.S., but that has fallen through. Henkel now is working out its next step, for acquiring detergent alcohols from whatever source for its U.S. operations; the company is tipped to be the partner for Celanese when Celanese retrofits its idle nylon-salts unit at Bay City, Tex., to make detergent alcohols from natural sources.

In theory, of course, naturals offer the lure of a continuing good raw material resource, renewable and manageable. But even the most enthusiastic boosters of the natural technology concede that it will be a long time before naturals return to a position of dominance over the industry or determine the pricing structure. There is simply too much synthetics capacity around now.

That is still quite a way into the future, though. More immediately, the reduction of phosphates is opening up a space in the detergent formulation that must be filled. Moreover, over the past few years, the percentage of surfactant in the formulation has been trimmed slightly, again opening room in the formulation. That, in turn, is putting increasing demand on producers of filler, or carrier, materials to help make up that 100% of product that goes in the detergent box. At the top of the list is sodium sulfate, a neutral, inert carrier for the active ingredients. Sodium carbonate could also be considered a filler, although it does have precipitating action against some water-hardness ions, so also functions as a builder. And in some products—laundry soap and detergent bars, for example—sodium bicarbonate is the filler of choice.

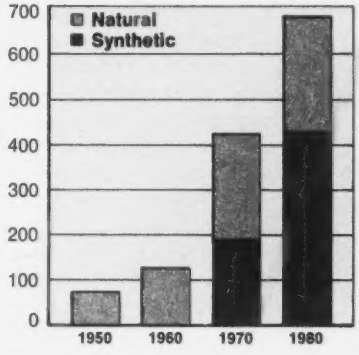
Soap bars and the increasingly popular synthetic detergent bars still are used heavily in developing countries. They provide concentrated detergents on the fabrics, with little waste, and are also easy to carry about. The other unusual—at least to western thinking—product form is found in Indonesia, which is a paste market. An error long ago in processing led to slurry-derived pastes of synthetic detergent being sold, and serendipitously, the Indonesian consumers liked the product. Paste it has remained ever since.

Indeed, perhaps because washing and doing the laundry are such a part of home life, habits tend to change only very slowly. Regulations could, presumably, force massive changes, but fortunately for the detergent industry, the industry has weathered governmental actions through shifts in ingredients, perhaps, but not drastic changes.

The major directives affecting the detergent industry from the European Economic Community, for example, have covered the biodegradability of surfactants. The first such directive in 1973 covered anionic surfactants, to ensure that all anionics used be 80% biodegradable. The next directive, published in 1982, provided similar rules for nonionic surfactants. And a third for cationics is still under discussion. The industry is covered by EEC regulations and directives on dangerous substances—what is being used in the formulation and what must therefore be put on the package label.

But by and large, most of the directives (a less sweeping, urgent form of action than a regulation with EEC) pertain to the category of

Synthetics dominate world output of fatty alcohols



Source: Industry estimates

Soap goes its own way

The industry tends to concentrate on the vast quantities and the more recent marketing excitement of the synthetic detergent part of the business. But soap continues to be a force that cannot be ignored.

This year, there will be an estimated 6.96 million metric tons of soaps used worldwide. Admittedly, that is down from the 7.87 million metric tons of eight years ago. And most of the use is in the developing countries. The detergent industry in South Korea, for example, is dominated by soaps, as are those in many African countries. And abundant supplies of natural fats—tallow, for example—can lead to political endorsement of soapmaking, as in Latin America.

Nevertheless, even in the U.S., this year about 500,000 metric tons of soap and soap products will be used.

In the U.K., soap is the base of one of the country's leading heavy-duty laundry detergents, Unilever's Persil. Sold as a formulated soap powder, such a product is well suited to the twin-tub machines that still account for slightly more than half the washing machines found in the U.K.

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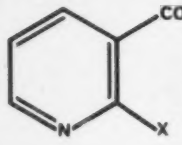
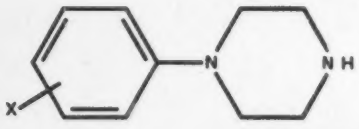


Substituted Nicotinic Acids



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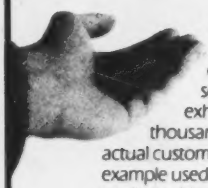

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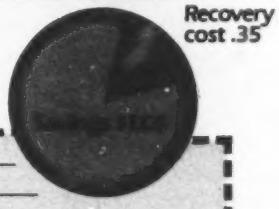

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packaging—determining package sizes, measuring weights and contents, and so on. Compared to everything else, that's merely a minor annoyance.

The soap and detergent industry over the past 40 years has gone through three major shifts. The earliest came shortly after World War II when the industry began a wholesale conversion to synthetic detergents, away from soap. The next shift was in the mid-1960s, away from branched-chain alkylbenzene sulfonates to the linear materials. The third was the march at least half way away from the anionic surfactants to the ethoxylated nonionic surfactants.

In two of those cases, the motion was welcomed by the industry—to synthetic detergents and to nonionics. But the other shift, away from branched-chain surfactants, was resisted early on by industry. Industry researchers at first were fighting the battle on suspected carcinogenicity grounds and only later realized the real front was biodegradability. The industry then voluntarily switched.

And now, the industry is in the midst of a fourth major shift, in the concerns over phosphates. Detergent makers argue that there is no strong move worldwide to ban phosphates from detergents because to do so would be too great a cost for the slight improvements in water quality that might result. These manufacturers have shown that in their industry publications, they say. But that misses a crucial point: Most consumers don't read industry publications, and environmentally active consumers don't believe such publications, no matter what their accuracy or truthfulness.

For the detergent industry, and for its suppliers, the present really important problems are those of capacities and profit margins. For suppliers, there is overcapacity for nearly all detergent intermediates. And much more likely than shutdowns of capacity is the prospect of more companies getting into the business—Celanese, for instance, with a retrofitted fatty alcohols plant soon to come on stream in the U.S., and Chimica Augusta under political pressure to reopen a now-closed al-

World production: growth is in developing countries

Thousands of metric tons	1976	1980	1984
North America	**5,398.7**	**5,432.0**	**5,530.6**
Soaps	507.3	532.7	557.1
Detergents	4,891.4	4,900.0	4,973.5
Western Europe	**5,298.4**	**6,064.0**	**6,575.0**
Soaps	891.8	823.4	765.8
Detergents	4,406.6	5,240.6	5,809.2
Eastern Europe	**2,962.0**	**2,736.8**	**2,750.0**
Soaps	1,273.7	1,171.8	1,120.7
Detergents	1,688.3	1,565.0	1,629.3
Latin America	**2,075.0**	**2,432.7**	**2,756.8**
Soaps	1,144.1	1,315.6	1,500.0
Detergents	930.9	1,117.1	1,256.8
Oceania	**252.4**	**265.6**	**281.5**
Soaps	57.0	65.6	72.2
Detergents	195.4	200.0	209.3
Africa	**960.9**	**1,243.6**	**1,492.3**
Soaps	677.6	847.0	1,010.0
Detergents	283.3	396.6	482.3
Asia	**4,866.6**	**4,668.2**	**4,969.7**
Soaps	3,317.2	2,421.6	1,936.8
Detergents	1,549.4	2,246.6	3,032.9
GRAND TOTAL	**21,814.0**	**22,842.9**	**24,355.9**
TOTAL SOAPS	**7,868.7**	**7,177.7**	**6,962.6**
TOTAL DETERGENTS	**13,945.3**	**15,664.9**	**17,393.3**

Note: Detergents figures include compounded soap powders. **Sources:** Henkel, C&EN estimates. Original data available from Association Internationale de la Savonnerie et de la Détergence, and from national governments' statistics

cohols plant in Italy, with new technology to reduce the branching in its alcohols. Union Carbide's pulling out of the linear alkylate merchant business last year was a rare, but for the industry, blessed, exception.

As one supplier says, although there is structural overcapacity, normal competitive pressures have brought a balance to the industry to give a livelihood for everyone. It's not good enough for reinvestment, he adds, but not bad enough to precipitate rationalization. However, any major changes can only bring the market into shambles.

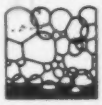
One of the hopes for intermediate suppliers is in price strengthening, but on the other side of the coin, detergent makers say they are hard-pressed to maintain margins, too. Competition from private-label and generic detergents has kept prices of the brand-name merchandise low, and in troubled economic times, consumers pinch their coppers.

The economy is picking up again around the world, nevertheless it will still be quite a while before anyone in the soap and detergent industry is making the "obscene profits" that many consumer activists love to rail against. □

Anionics dominate U.S. surfactant production

Millions of lb	1982 Production	1982 Merchant sales	1982 Sales value ($ millions)
AMPHOTERIC	**25.1**	**26.2**	**$ 28.2**
ANIONIC	**3054.8**	**1499.0**	**501.4**
Carboxylic acids and salts	802.6	121.6	77.5
Phosphoric and polyphosphoric acid esters and salts	28.9	23.4	21.9
Sulfonic acids and salts	1634.7	1118.5	254.9
Sulfuric acid esters and salts	536.7	206.5	130.8
Other	51.9	29.0	16.3
CATIONIC	**380.1**	**295.6**	**246.1**
Amine oxides and oxygen-containing amines	83.1	32.5	31.3
Amines and amine oxides	46.1	34.1	26.7
Amines not containing oxygen	61.8	55.7	53.4
Quaternary ammonium salts	155.7	141.8	109.0
Other	33.4	31.5	25.7
NONIONIC	**907.2**	**774.2**	**472.5**
Carboxylic acid amides	58.3	49.0	46.1
Carboxylic acid esters	210.3	171.6	130.9
Ethers	591.9	539.7	284.1
Other	46.7	13.9	11.4
TOTAL	**4367.2**	**2595.0**	**$1248.2**

Source: International Trade Commission



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Rule 3. Water hardness inhibits lathering.

HAMPOSYL Surfactants give rich creamy lathers and are richer in hard water.

Rule 4. Specialty surfactants cost lots of money.

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